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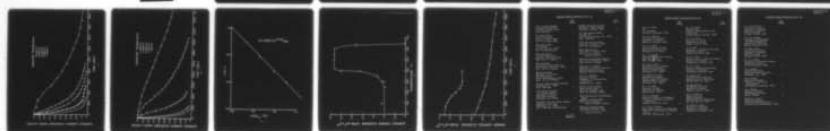
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THE DISSOLUTION OF CARBON ADLAYERS INTO THE (110) FACE OF NICKE--ETC(U)
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TECHNICAL REPORT NO.6

THE DISSOLUTION OF CARBON ADLAYERS
INTO THE (110) FACE OF NICKEL

by

Radhesyam Sau and John B. Hudson

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ABSTRACT

The rate of carbon dissolution from adsorbed layers through the (110) face of a nickel crystal has been measured for a wide range of initial surface carbon concentrations over the temperature range from 600 to 913K. Auger electron spectrometry was used to measure the decrease in surface carbon concentration with time at temperature. For graphitic monolayers at $T > 873\text{K}$, dissolution is controlled by the transport of carbon from adsorbed layer to bulk. For dilute adlayers at $T \approx 723\text{K}$, dissolution is controlled by the bulk diffusion rate of carbon. At intermediate values of initial carbon concentration and temperature, quantitative treatment of the dissolution rate was not possible.

INTRODUCTION

There have been several recent studies of the thermodynamic and kinetic behavior of carbon adlayers on the various faces of nickel. The works of Blakely et al.^{1,2,3} are typical of the thermodynamic studies. The kinetics have been studied qualitatively by Sickafus⁴ and more recently by Schouten et al.⁵ The thermodynamic studies generally indicate the presence of multiple adlayer phases. High concentration surface layers, in some cases having a carbon-carbon spacing typical of C-face graphite, are stable at low temperatures and high bulk carbon concentrations. At higher temperatures and/or low bulk carbon concentrations, a dilute adlayer phase is in equilibrium with the bulk.

In the work of Sickafus, the disappearance of surface carbon from a Ni(110) surface was studied by Auger spectroscopy. The author concluded that the removal mechanism involved reaction of surface carbon with residual oxygen-containing gases in the system and thus his results do not bear on the question of dissolution kinetics directly. In the work of Schouten et al. dissolution of carbon from a Ni(110)-(2x3)-C structure was observed, also by Auger spectroscopy, in the temperature range between 618-658K. In this case, the authors conclude that the rate-controlling step in the dissolution process was the bulk diffusion of carbon into the interior of the crystal, with local equilibrium being maintained between the surface and the near-surface bulk.

We have measured the dissolution kinetics of carbon from both carbidic and graphitic monolayer adsorbed phases into the Ni(110) surface, in the temperature range between 600 and 920K. We find, in the case of graphitic layers that the dissolution rate is controlled by surface processes that are slow compared to bulk diffusion.

EXPERIMENTAL

The measurements to be described were carried out in an all-metal, ion-pumped ultrahigh vacuum surface research system described in detail elsewhere.⁶ Components of the system pertinent to the present study include a universal sample positioner, which provides for specimen mounting and temperature control, a cylindrical mirror analyzer (CMA) for measurement of sample surface composition by Auger electron spectroscopy (AES), an auxiliary vacuum chamber which permitted dosing of the sample surface with a molecular beam of ethylene, and an ion gun which was used to clean the surface by argon ion bombardment and anneal between experimental runs.

The sample was the same (110) oriented nickel single crystal used in previous studies in this system. It was a ribbon crystal, 2.5cm by 0.67 by 0.025 cm thick, with a (110) orientation on the flat surface, and was heated resistively with a.c. Temperature measurement was accomplished by a W-5%Re vs. W-26%Re thermocouple spotwelded to the sample, and calibrated by comparison with a calibrated optical pyrometer in the temperature range from 1000-1300K.

The surface carbon layer was prepared by first cleaning the sample surface by ion bombardment and anneal until AES showed no peaks other than those characteristic of nickel. The sample was then exposed, at a temperature between 575 and 775°K to an ethylene molecular beam until the desired level of the carbon AES signal was observed. Previous results⁶ indicate that saturation exposure at 775°K leads to formation of a carbon layer having the carbon-carbon spacing typical of the C-face of graphite, namely a surface carbon concentration of 3.35×10^{15} carbon atom/cm². Saturation exposure at 575°K leads to a layer having 1.1×10^{15} carbon atom/cm². This layer undoubtedly represents a surface carbide structure observed previously by others.^{7,8}

After the carbon layer had been formed, the sample temperature was raised to the desired annealing point. The peak-to-peak height of the carbon Auger peak at 273 volts was then monitored as a function of time to determine the rate of dissolution of the layer. For the case of the graphitic layer, measurements were made at 10°C increments between 753 and 813K. The dissolution process was too slow at lower temperatures to permit measurements to be made in a reasonable amount of time. Measurements were also made at lower temperatures on the carbidic layers.

RESULTS AND ANALYSIS

1. Graphitic Layers

The resulting data on surface carbon concentration, taken as being proportional to the peak-to-peak height of the carbon Auger feature, are plotted as a function of annealing time for the various temperatures measured in Figures 1 and 2. The times required for dissolution are in all cases on the order of hundreds of seconds. This immediately rules out bulk diffusion as the rate controlling process. If one accepts the values of Diamond and Wert⁹ for bulk diffusion of carbon in nickel, and the solubility relation found by Natesan and Kassner,¹⁰ and makes the assumption that the dissolution reaction at the surface is not rate controlling, then one determines that the rate of the dissolution process should follow the relation

$$\theta_c = \theta_i - \left[(2 \times 10^{21}) e^{\left(\frac{-13750}{T} \right)} t^{1/2} \right] .$$

in which θ_i and θ_c are the initial and instantaneous value of surface carbon coverage (atom/cm²) and t is time. Behavior following this relation would result in a decrease in carbon coverage to below detectability by AES in less than one second at the lowest temperature used here.

The dissolution process must thus be controlled by an interfacial reaction step. At high temperatures (above 883K) the dissolution curves are fit very well by a first-order decomposition reaction equation, i.e.

$$\theta_c = \theta_i \exp(-kt),$$

The values of k obtained from this analysis are summarized in Table 1. An Arrhenius plot of those values leads to an activation energy for the dissolution process of 89 Kcal/mol. This figure appears reasonable, in that it is greater than the heat of solution of carbon in nickel (endothermic by 10 Kcal/mol¹⁰), but is considerably smaller than the heat of vaporization of graphite (170 Kcal/mol¹¹).

The dissolution behavior at lower temperatures is markedly different than that at high temperatures. It can be seen from Figures 1 and 2 that the dissolution curves taken below 883K are qualitatively different from those at higher temperatures, being concave downward at short dissolution times. Such a shape is not consistent with a first-order reaction mechanism. The temperature at which the change in kinetic behavior is observed coincides with the temperature at which the graphitic layer becomes stable on the surface, as shown in Figure 4. This is a plot of the steady-state surface carbon coverage as a function of temperature, taken during exposure of the nickel surface to the ethylene molecular beam. This implies equilibrium between the graphitic layer and the near-surface bulk at ~873K. The much slower removal of carbon at this temperature and below must be associated with another reaction, either slow reaction with oxygen-containing residual gases, as was apparently the case in the work of Sicakfus, or a gradual destabilization of the graphitic layer due to reduction in the near-surface carbon concentration by long-range bulk diffusion of carbon.

2. Carbodic Layers

We have made limited measurements of the rate of dissolution of carbodic adlayers having initial coverages $\theta_c \leq 1.1 \times 10^{15} \text{ atom/cm}^2$. These measurements were made primarily to provide a comparison with the previous work of Schouten et al.⁵ The dissolution curves shown in Figure 5 are typical of those obtained for carbide layers. The upper curve, taken for $\theta_i = 1.1 \times 10^{15} \text{ atom/cm}^2$, shows a very low initial rate, followed by a more rapid decrease and a leveling off at a level of $8 \times 10^{14} \text{ atom/cm}^2$. We feel that this represents competition between dissolution into the bulk, and formation of the surface graphitic layer, which, as can be seen from Figure 4, is the stable surface phase at the temperature of measurement. The low dissolution rate for this layer relative to that of the lower concentration layer discussed below is most probably due to carbon-carbon interactions in the layer. The curve for $\theta_i = 5.5 \times 10^{14}$, a value closer to those used by Schouten et al., follows the $t^{1/2}$ dependence found by these authors, but at a much slower rate. Their data may be brought into correspondence with ours by assuming an error in temperature measurement on the part of one set of experimenters. That is, our results at 723K coincide with their results at ~658K. No estimate is given of the possible temperature error in the previous work of Schouten et al.¹² In the present work, as mentioned earlier, the thermocouple was calibrated using an optical pyrometer focussed on the region of the crystal that was exposed to the ethylene molecular beam. We estimate that this procedure yields temperatures accurate within 20°C.

Another possible source of discrepancy is the reaction of surface carbon with dissolved oxygen. In one set of measurements, oxygen was adsorbed on the nickel surface, then dissolved into the bulk by heating at 900K. The dissolution rate of carbon adlayers having $\theta_i = 1.1 \times 10^{15} \text{ atom/cm}^2$ was measured at 425°C on this surface and on surfaces not previously exposed to oxygen. The

dissolution rate was unmeasurably small in the latter case, but rapid (half the carbon removed in 400 sec.) on the oxygen-treated surface.

SUMMARY

The rate of carbon dissolution into the Ni(110) surface is a complicated function of temperature, initial surface carbon coverage and initial near-surface bulk carbon and oxygen coverages. In carbon layers having an initial concentration of 1.1×10^{15} atom/cm or higher, carbon-carbon interactions limit the rate of the dissolution. In the extreme case of graphitic layers at temperatures above 880K, the dissolution rate can be explained quantitatively in terms of the energy required to remove a carbon atom from the graphitic layer.

At the lowest temperatures and carbon concentrations studied, as was the case in the work of Schouten et al.⁵, bulk diffusion of carbon appears to be rate controlling.

In the intermediate range of temperature and initial carbon concentration the interplay of factors such as carbon-carbon interactions within the adlayer, the stability of various adlayer phases relative to bulk phases and to each other and the effects of significant bulk concentrations of carbon or oxygen do not permit quantitative treatment of the dissolution process.

ACKNOWLEDGEMENT

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FIGURE CAPTIONS

1. Carbon dissolution rate curves - graphitic layers at high temperatures:
2. Carbon dissolution rate curves - graphitic layers at low temperatures:
3. Arrhenius plot of first order reaction rate constant for carbon dissolution from graphitic monolayer.
4. Steady state surface carbon concentration vs. temperature for Ni(110) surface exposed to ethylene molecular beam. Beam flux $\approx 10^{14}$ molec/cm²sec.
5. Carbon dissolution rate curves - carbidic layers.

TABLE 1

<u>Temperature - °K</u>	<u>Dissolution Rate Constant - Sec⁻¹</u>
883	3.21×10^{-3}
893	5.10×10^{-3}
903	9.20×10^{-3}
913	17.2×10^{-3}

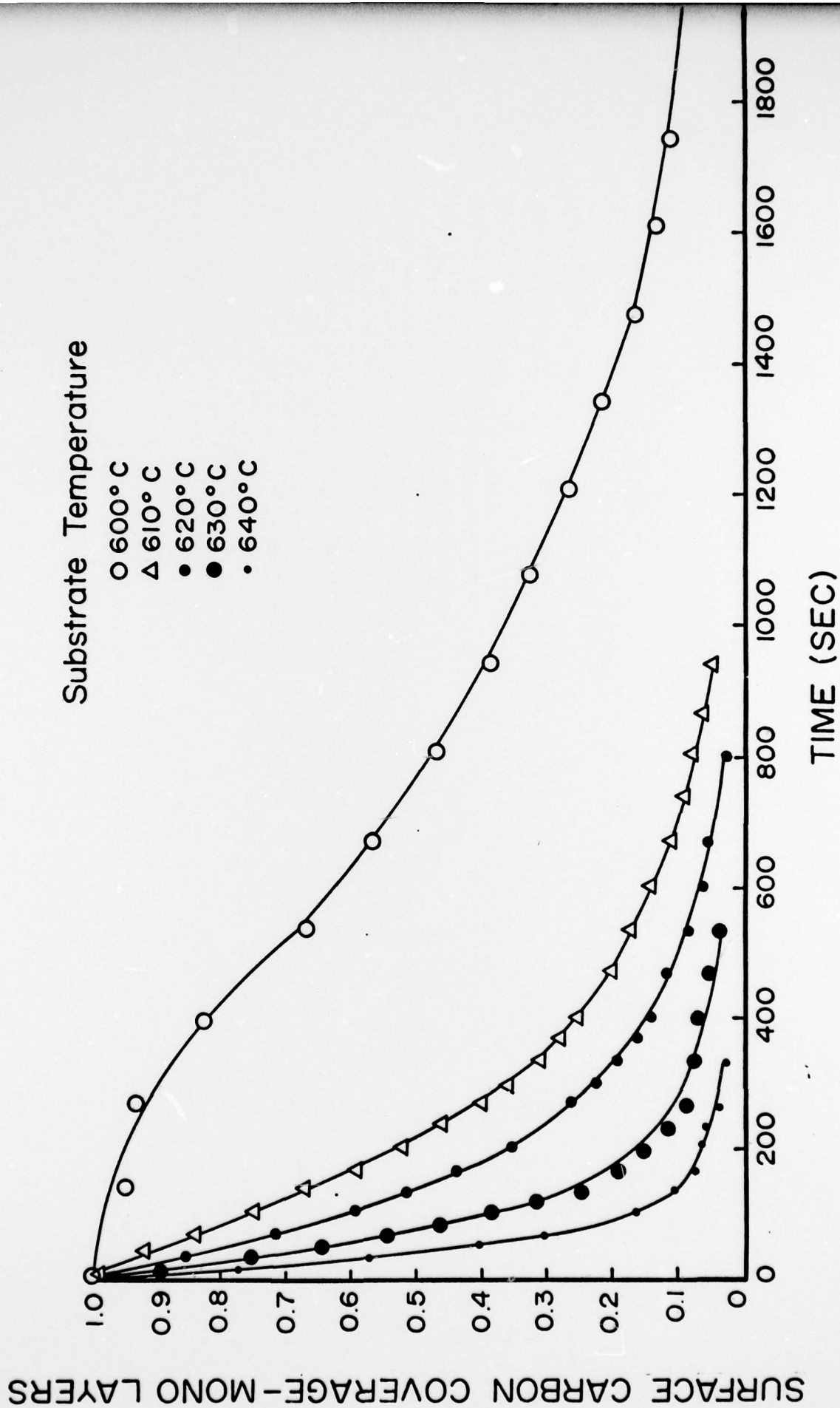


FIG. 1

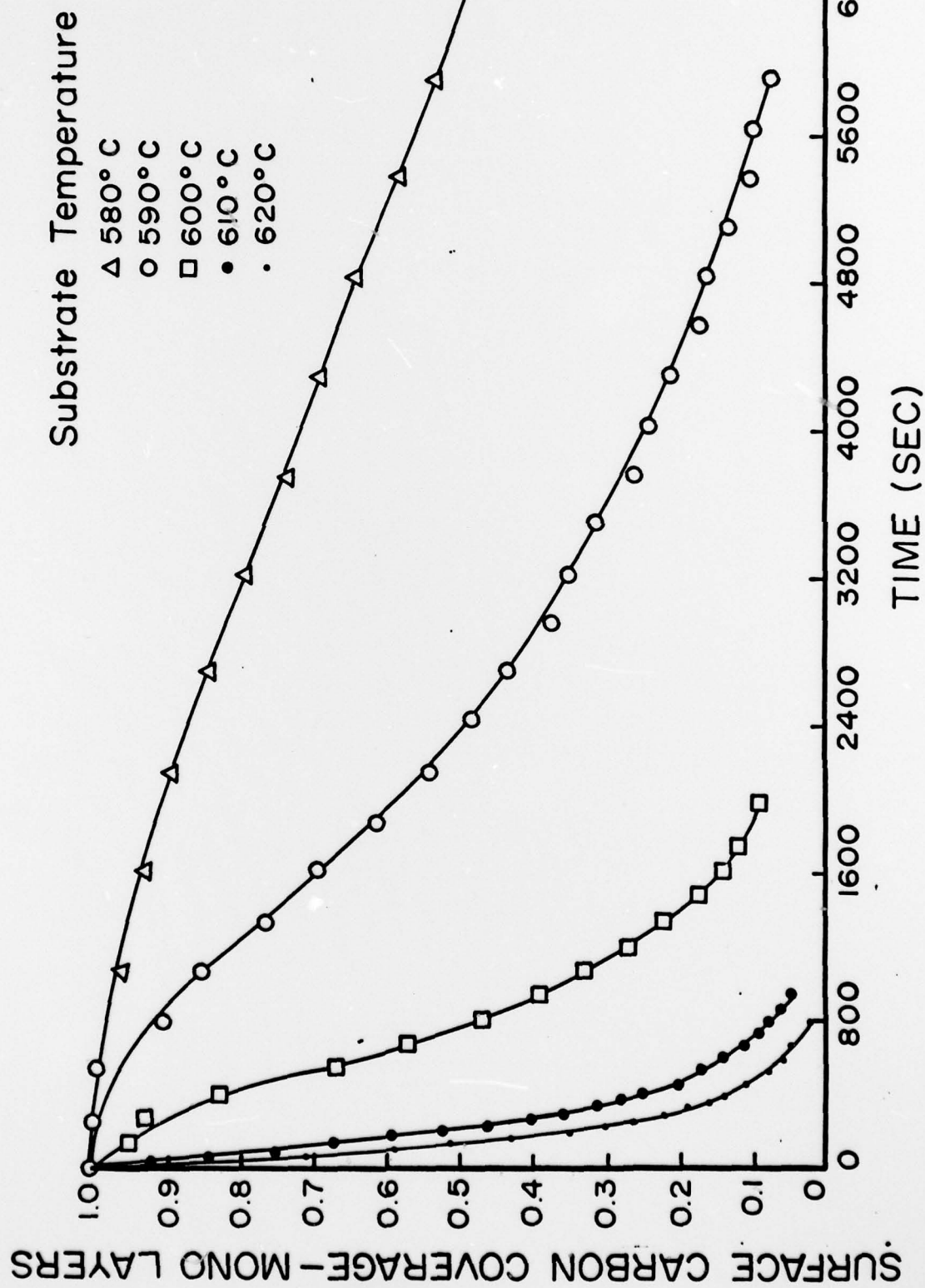


FIG. 2

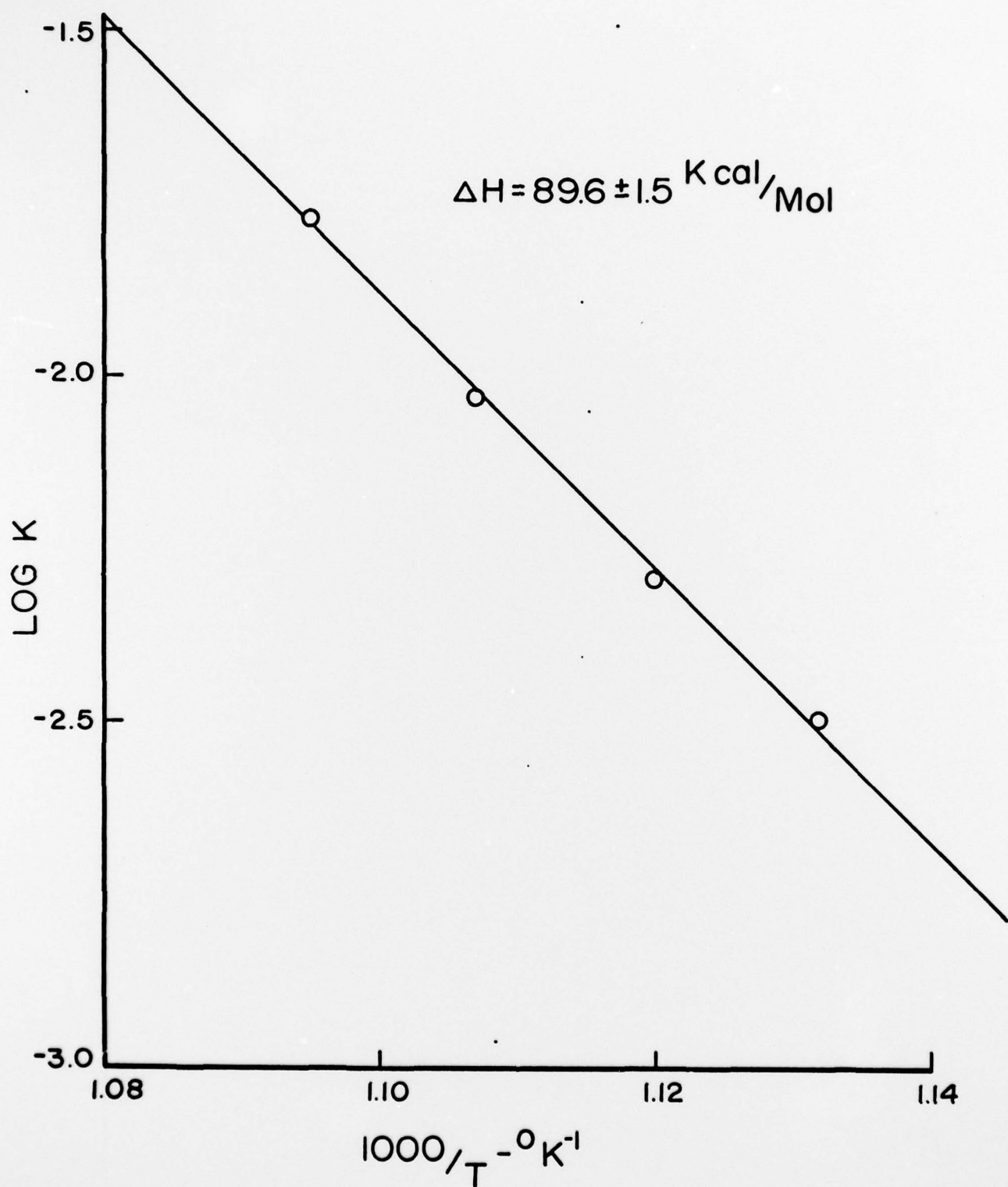


FIG. 3

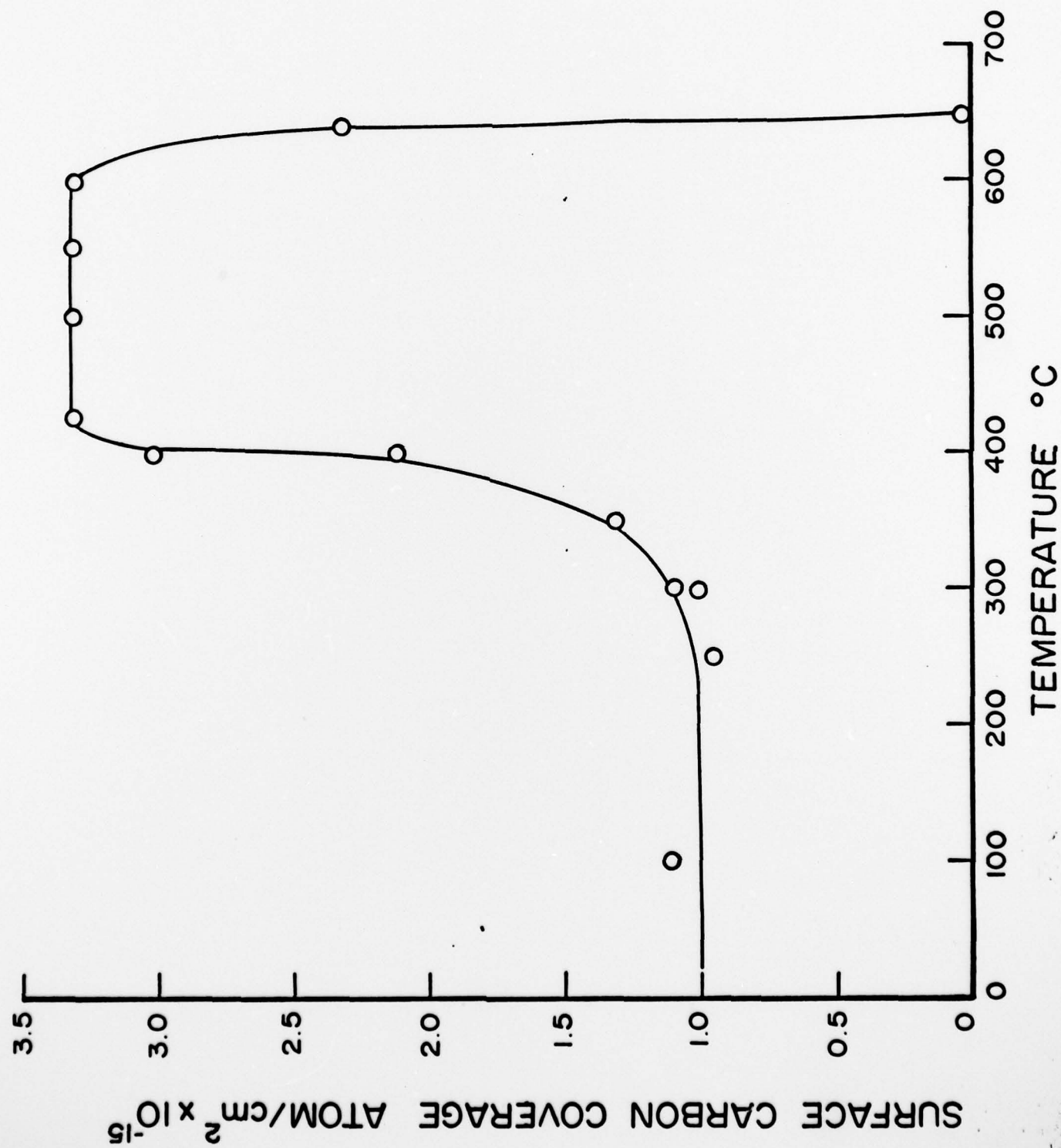


FIG. 4

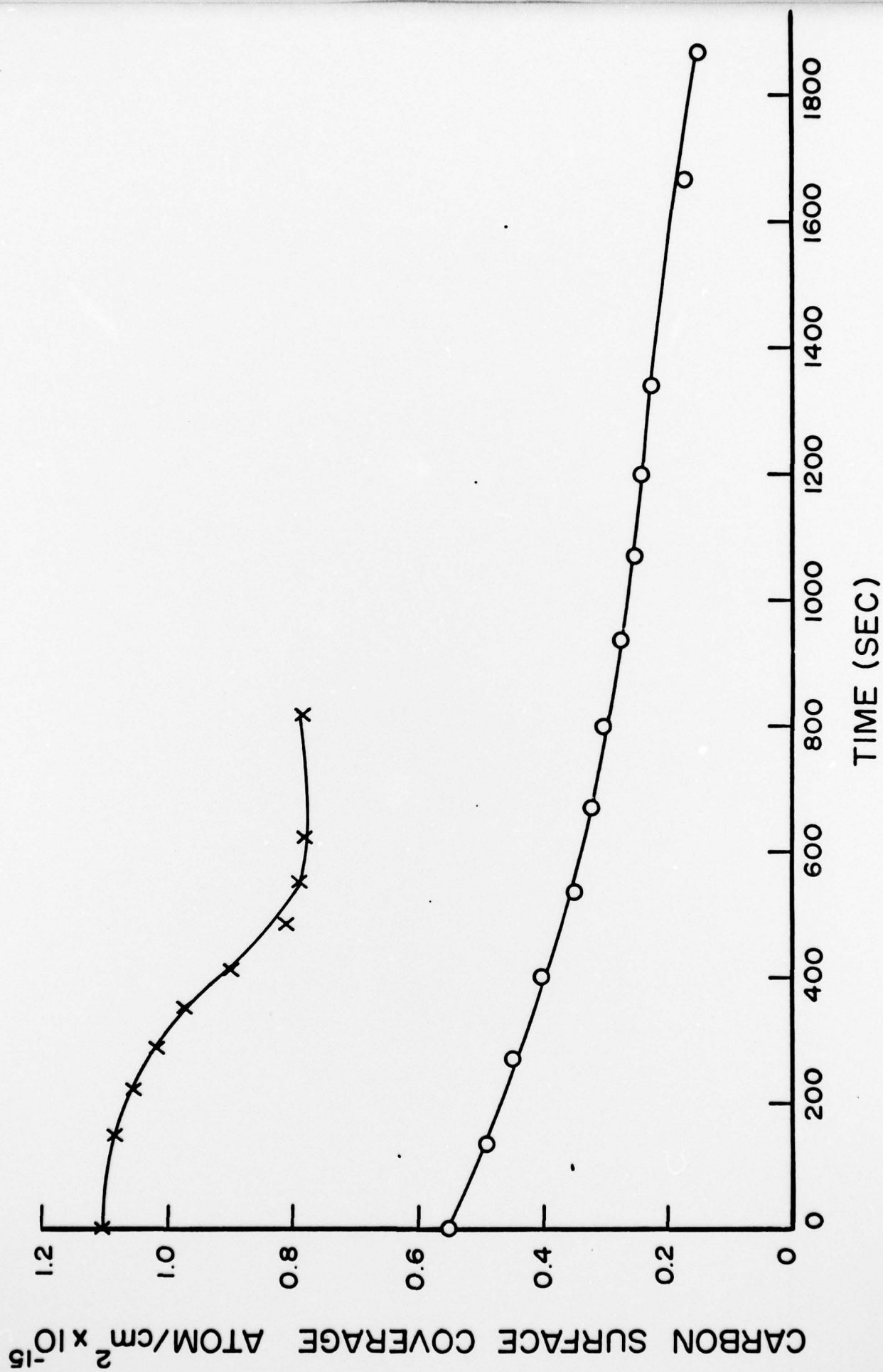


FIG. 5

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